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Stereoselective Association between Acetylacetonatobis(ethylenediamine)cobalt(III) and Malonate Ions as Studied by Nuclear Magnetic Resonance[1)]

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The effect of added malonate upon the chemical shift and the exchange rate of amine hydrogens of acetylacetonatobis(ethylenediamine)cobalt(III) ion, $[Co(acac)(en)_2]^{2+}$, have been investigated by ^1H and ^{13}C NMR spectroscopy. In the absence of malonate, the amine groups give rise to two signals in the ^1H spectra and two rate constants of amine exchange due to *trans* and *cis* (to coordinated oxygen) amine groups. Upon addition of malonate, the *trans* NH_2 undergoes a down-field shift, the *cis* NH_2 resonance splitting into two peaks. In the presence of malonate, all of the four kinds of amine hydrogens of $[Co(acac)(en)_2]^{2+}$ exhibit different exchange rates. The following conclusion was obtained from the results coupled with ^{13}C NMR data. (i) The malonate ion works in two ways in amine exchange, as a general base catalyst and to form an exchange-inert ion-pair. (ii) The two *trans* hydrogens that are directed approximately parallel to the two-fold axis of the complex ion hydrogen-bond simultaneously to the two carboxyl groups of malonate, leading to a retardation of amine exchange rates. (iii) The rates of the other *trans* hydrogens and *cis* hydrogens are determined by a compromise between acceleration due to general base catalysis and deceleration due to forming ion-associated species. (iv) The conformation of coordinated ethylenediamine is fixed as either (δδ) or (λλ) in the hydrogen-bonded species.

The amine groups of *cis*-$[CoX_2(en)_2]^+$ ions give rise to two broad singlets in their proton NMR spectra. However, the assignment of these singlets to *cis* and *trans* amines, which are *cis* and *trans* to coordinated X ligands, respectively, is not straightforward owing to their equal intensities. A method of assigning these signals on the assumption that the chemical shifts of amine hydrogens are determined primarily by the magnetic anisotropy of the central cobalt(III) ion was proposed.[2)] Although the theory based on the magnetic anisotropy could explain the chemical shift variations for a series of pentaamminecobalt(III) ions, the agreement was not good for *cis*-$[CoX_2(en)_2]^+$ type of complexes.

While ion-associated species in solution are believed to have well-defined structures, little evidence seems to have been obtained, particularly in the case of diamagnetic metal complexes.[3)] A limited number of structures of ion-pairs in solution are proposed[4)] mainly from studies of circular dichroism spectra. The circular dichroism technique is limited to optically active compounds. The kinetic behavior of amine hydrogen exchange of *cis*-$[CoX_2(en)_2]^+$ ions might be affected by added anions. Thus stereochemical information obtained from the effects of added anions on the hydrogen exchange kinetics, could be applied to many complexes irrespective of optically active and inactive complexes.

The aim of this work is twofold: (a) to obtain evidence in support of the postulated NMR assignments and (b) to obtain stereochemical information on the ion-paired species. We chose the system $[Co(acac)(en)_2]^{2+}$ and malonate, mal^{2-} for the following reason. Since the cation carries a higher positive charge than most *cis*-$[CoX_2(en)_2]^+$ compounds which are usually univalent, it will interact more strongly with added anions and the effects of ion association would be significant.

Experimental

$[Co(acac)(en)_2]I_2 \cdot H_2O$ was prepapared and recrystallized analytically pure.[5)] Extra pure sodium malonate (Katayama Kagaku Kogyo Co. Ltd.) was used without further recrystallization. Sample solutions were made by dissolving the materials in D_2O (Merck, 99.75 atom % D minimum). The concentration of $[Co(acac)(en)_2]I_2$ of all solutions was 0.1 mol dm^{-3} and that of Na$_2$mal was varied from 0 to 1.0 mol dm^{-3} at suitable intervals.

^1H NMR spectra were measured on a Varian T-60 spectrometer operating at 60 MHz. The rate of amine hydrogen exchange was determined by measuring the NMR signal intensities of *cis* NH_2 and *trans* NH_2 at suitable time intervals. Proton chemical shifts are referred to internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate, DSS. All measurements were made at 36.4 °C. Proton noise decoupled and undecoupled ^{13}C NMR spectra were recorded for H_2O solutions at 22.6 MHz on a Hitachi R-42 spectrometer by the FT technique. The pH of the sample solution was measured with a Hitachi-Horiba Model F-7 pH meter using a microelectrode immediately after kinetic measurements.

Results

Chemical Shifts. The ^1H NMR spectra of $[Co(acac)(en)_2]I_2$ in D_2O contain two broad signals at 5.02 ppm and 4.42 ppm from internal DSS, due to *cis* NH_2 and *trans* NH_2, respectively, which denote amine hydrogens *cis* and *trans* to oxygen atoms of coordinated acetylacetone.

Figure 1 shows the amine hydrogen portion of the ^1H NMR spectra of $[Co(acac)(en)_2]I_2$ with 0, 0.4, 0.8, and 1.0 mol dm^{-3} of Na$_2$mal taken immediately after dissolution in D_2O. Chemical shift values of each peak are given in Table 1. With an increase in the concentration of Na$_2$mal, the signal of *trans* NH_2 shifted to low fields. While *cis* NH_2 appeared as a single peak in the absence of Na$_2$mal, the *cis* peak became broader, its height being almost half of that of *trans* NH_2 when 0.4

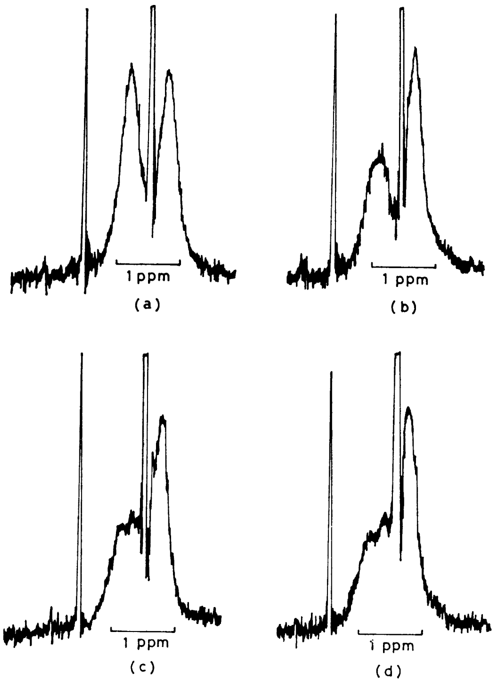


Fig. 1. The amine hydrogen portion of the ^{1}H NMR spectra of $[Co(acac)(en)_2]I_2$ with 0 (a), 0.4 (b), 0.8 (c), and 1.0 mol dm^{-3} (d) of Na_2mal, taken immediately after dissolution in D_2O. The strong central singlet is due to solvent HDO and to the left of the spectrum is the methine hydrogen of acac.

TABLE 1. ^{1}H CHEMICAL SHIFTS IN δ(ppm) FROM INTERNAL DSS FOR *cis* AND *trans* NH_2

Two peaks appear for *cis* NH_2 when Na_2mal exceeds 0.4 mol dm^{-3}.

Na_2mal (mol dm^{-3})	0	0.4	0.8	1.0
cis NH_2	5.02	5.07	5.11	5.13
		4.97	4.90	4.89
trans NH_2	4.42	4.47	4.52	4.53

mol dm^{-3} of Na_2mal was added. With 0.8 and 1.0 mol dm^{-3} of Na_2mal, the *cis* resonance eventually split into two peaks. The chemical shift difference of these two peaks increased with increasing concentration of Na_2mal. However, the average of their chemical shift values remained unaffected, being equal to the position of *cis* NH_2 without Na_2mal. The ^{13}C chemical shifts of $[Co(acac)(en)_2]I_2$ in the absence and presence of Na_2mal, referred to the methyl carbon resonance of internal methanol, are given in Table 2. The assignment was based on the splitting pattern of each resonance in the undecoupled spectrum.

Rates of Amine Hydrogen Exchange. In the absence of Na_2mal, the plots of ln(intensity) *vs.* time were linear for both *cis* and *trans* NH_2. The result for the solution with 0.1 mol dm^{-3} Na_2mal is shown in Fig. 2, where plots for *trans* NH_2 turn out to be a curve in contrast with a straight line for *cis* NH_2. Analysis of the rate data for *trans* NH_2 gave two pseudo-first-order rate

TABLE 2. ^{13}C CHEMICAL SHIFTS IN ppm OF $[Co(acac)(en)_2]I_2$ IN H_2O REFERRED TO THE METHYL CARBON OF INTERNAL METHANOL

The concentration of $[Co(acac)(en)_2]I_2$ and Na_2mal is 0.1 and 1.0 mol dm^{-3}, respectively. s, d, t, and q stand for singlet, doublet, triplet, and quartet signals in proton coupled spectra.

	CO(acac)	$COO^-(mal^{2-})$	CH(acac)	CH_3OH	$CH_2(mal^{2-})$	CH_2(en)	CH_2(en)	CH_3(acac)
Without Na_2mal	142.67(s)	——	49.45(q)	0	——	−3.77(t)	−5.66(t)	−22.83(q)
With Na_2mal	142.50(s)	128.02(s)	no signal	0	−2.06(t)	−3.86(t)	−5.75(t)	−22.83(q)

TABLE 3. FIRST-ORDER RATE CONSTANTS (s^{-1})

$k_{t(f)}$ and $k_{t(s)}$ denote faster and slower rate constants of *trans* NH_2, respectively. Without Na_2mal only one rate is obtained. $k_{c(L)}$ and $k_{c(H)}$ denote *cis* NH_2 when appeared separately at lower and higher fields, respectively. The signal of *cis* NH_2 does not split into two peaks when Na_2mal is 0 and 0.1 mol dm^{-3}.

Na_2mal (mol dm^{-3})	0	0.1	0.1	0.4	0.4
Apparent pH	6.72	6.18	6.44	5.91	5.80
$k_{t(f)}$	1.31×10^{-3}	2.89×10^{-3}	2.55×10^{-3}	9.78×10^{-4}	5.69×10^{-4}
$k_{t(s)}$		4.88×10^{-4}	5.29×10^{-4}	8.00×10^{-5}	7.80×10^{-5}
$k_{c(L)}$	4.57×10^{-4}	3.48×10^{-4}	3.23×10^{-4}	1.70×10^{-4}	7.54×10^{-5}
$k_{c(H)}$					2.15×10^{-5}

Na_2mal (mol dm^{-3})	0.6	0.6	0.8	0.8	1.0
Apparent pH	5.99	5.93	5.84	5.84	5.88
$k_{t(f)}$	7.70×10^{-4}	9.06×10^{-4}	5.29×10^{-4}		
$k_{t(s)}$	7.28×10^{-5}	8.53×10^{-5}	8.10×10^{-5}		
$k_{c(L)}$	8.67×10^{-5}	1.33×10^{-4}	7.73×10^{-5}	8.60×10^{-5}	7.35×10^{-5}
$k_{c(H)}$	6.47×10^{-5}	1.08×10^{-4}	2.44×10^{-5}	4.77×10^{-5}	4.02×10^{-5}

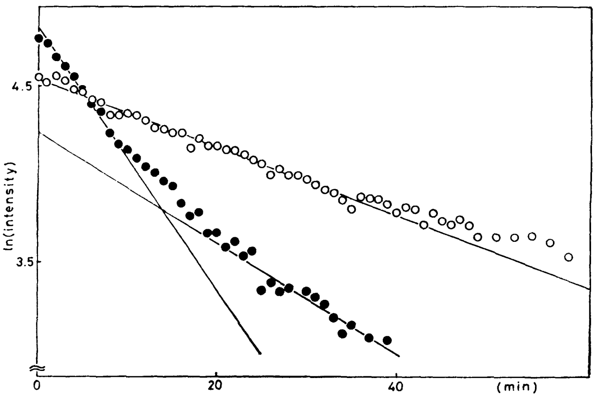


Fig. 2. The plots of ln (intensity) *vs.* time for *cis* (○) and *trans* (●) NH_2 of $[Co(acac)(en)_2]^{2+}$ with 0.1 mol dm^{-3} of Na_2mal.

constants $k_{t(f)}$ and $k_{t(s)}$, which denote faster and slower exchange rates of *trans* NH_2, respectively. The rate constants with varying concentration of Na_2mal are given in Table 3, along with apparent pH. The *trans* NH_2 peak underwent a down-field shift with Na_2mal and at 0.8 mol dm^{-3} of Na_2mal was too close to the strong HDO peak, making the measurement difficult. Since the *cis* resonance splits into two peaks when the Na_2mal concentration exceeds *ca.* 0.5 mol dm^{-3}, two rate constants, $k_{c(H)}$ and $k_{c(L)}$, refer to the peaks at higher and lower magnetic fields, respectively.

Discussion

The Assignment of Amine Signals. In a previous paper a method was proposed for assigning two NH_2 signals of *cis*-$[CoX_2(en)_2]^+$ ions.[2] It was based on the assumption that the chemical shifts of amine hydrogens are primarily determined by the magnetic anisotropy of the central cobalt(III) ion. It has been proposed that for *cis*-$[CoX_2(en)_2]^+$ ions the *cis* NH_2 resonates at a field lower than the *trans* NH_2 if the ligand X is ranked lower, like acac, than en in the spectrochemical series. Thus the *trans* NH_2 of $[Co(acac)(en)_2]^{2+}$ is expected to appear at higher magnetic field than the *cis* NH_2. On the other hand, in a kinetic study of amine hydrogen exchange for several *cis*-$[CoX_2(en)_2]^+$ type of complexes,[6] it was found that the *trans* amine hydrogens are exchanged much faster than the *cis* hydrogens if X is a weaker ligand than en (acac is an example). In the absence of malonate the high field NH_2 signal decreased in intensity more rapidly than the low field one, indicating assignment of the high field signal to the *trans* NH_2.

The results suggest that the high field resonance at δ 4.42 is due to the *trans* NH_2 of $[Co(acac)(en)_2]^{2+}$. The effect of added malonate on amine exchange kinetics can be consistent only when we adopt this assignment.

HD Exchange Kinetics. The *trans* NH_2 exhibits two exchange rates in the presence of Na_2mal, in contrast with only one rate in the absence of malonate. This indicates that two kinds of hydrogens of *trans* NH_2 are discriminated by mal^{2-} in solution. A molecular model shows that *trans* NH_2 has two kinds of hydrogens, H_A (pointing approximately parallel to the molecular two-fold axis of $[Co(acac)(en)_2]^{2+}$) and H_B, and that two carboxyl groups of mal^{2-} can hydrogen-bond simultaneously to two H_A's (Fig. 3). It is reasonable that mal^{2-} approaches the complex electrostatically from the side opposite acac along the two-fold axis because minus charge is localized on acac. The shift of *trans* NH_2 to low fields caused by addition of Na_2mal supports this view since hydrogen bonding causes downfield shifts.[7] We thus assign the slower exchange rate, $k_{t(s)}$, to H_A and the faster one, $k_{t(f)}$, to H_B. Since double hydrogen bonding would greatly stabilize the chelate structure, we might expect that *trans* H_A is not exchanged while retaining the hydrogen bond.[8]

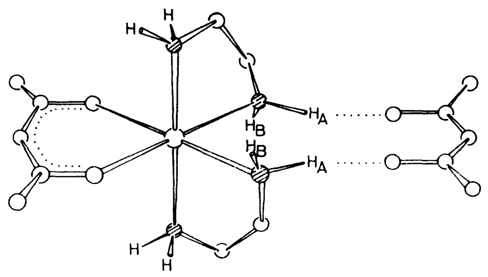


Fig. 3. The proposed structure of ion-associated species, $[Co(acac)(en)_2]^{2+}\cdots\cdots mal^{2-}$.
H_A is approximately parallel to the C_2-axis. Malonate ion approaches from the side opposite to acac along the C_2-axis and hydrogen bonds only to H_A.

HD exchange rate constants of coordinated amine groups are proportional to the concentration of OD^- ion.[9]

$$k \propto [OD^-]$$

The equation still holds for such situations where a stable ion-associated species is formed between the metal complex and added anions. In such cases the second-order rate constant $k'=k/[OD^-]$ decreases gradually with an increasing anion concentration. This has been ascribed to an increase in the number of ion-associated species for which amine hydrogen exchange is considered extremely slow. Yamatera and Fujita[10] utilized this behavior to obtain the association constant between Λ- and Δ-$[Co(en)_3]^{3+}$ and *d*-tartrate ions. Their result can be rationalized by invoking the face-to-face multifunctional hydrogen bonding in solution, as found in the crystal structure of Λ-$[Co(en)_3]Br$(*d*-tartrate)$\cdot 5H_2O$.[11] We will discuss our results in terms of the second-order rate constants $k'_i=k_i/[OD^-]$ (i=c, t(s), t(f)), which were derived by using $K_w(D_2O)$,[12,13] corrected according to the ionic strength of the solution extending from 0.3 to 2.5. k' values were plotted against $[Na_2mal]/[complex]$ in order to see the dependence of k' on the concentration of malonate (Fig. 4).

The $k'_{t(f)}$ values for *trans* H_B increase sharply upon addition of Na_2mal, followed by a gradual decrease in the concentration of Na_2mal. Since the rate enhancement can not be due to pH-effect, mal^{2-} and $Hmal^-$ work as general base catalysts, enhancing the rate of *trans* H_B. This may be performed through an ion-pair such as

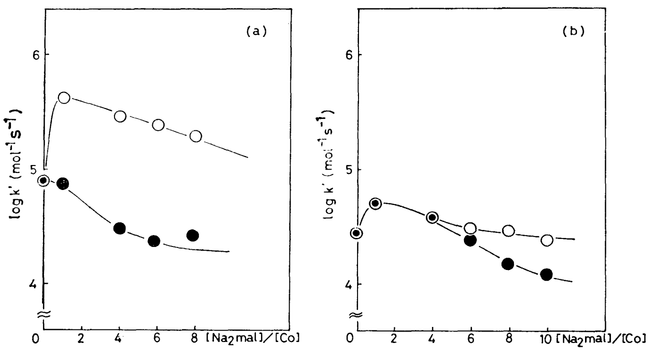
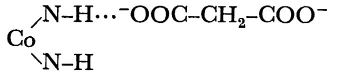


Fig. 4. The plots of logarithms of second-order rate constants ($mol^{-1}\ s^{-1}$) *vs.* the molar concentration ratio of Na_2mal to $[Co(acac)\ (en)_2]I_2$.
(a) For *trans* NH_2; Two rates, $k'_{t(f)}$ (○) and $k'_{t(s)}$ (●), are detected in the presence of Na_2mal. (b) For *cis* NH_2; Addition of Na_2mal brought about a splitting of the *cis* peak into two peaks, hence $k'_{c(L)}$ (○) and $k'_{c(H)}$ (●).



$$Co\begin{matrix}\nearrow N\text{-}H\cdots{}^{-}OOC\text{-}CH_2\text{-}COO^{-}\\ \searrow N\text{-}H\end{matrix}$$

where one of the carboxyl groups hydrogen-bonds to an amino group, the other dangling and not interacting with amino hydrogens. A similar rate enhancement due to general base catalysis by acetate and malonate has been confirmed for *cis*-$[CoX_2(en)_2]^+$ ions with X_2= mal^{2-}, $(CN)_2$, $(NO_2)_2$.[14] The gradual reduction of $k'_{t(f)}$ may be interpreted as follows. The number of predominant ion-associated species increases with an increase in the concentration of malonate (Fig. 3). Since associated species have zero electric charge, it is improbable that mal^{2-} or $Hmal^-$ ion approaches this associated species, acting as general base catalysis on the associated complexes.

The $k'_{t(s)}$ value, which refers to *trans* H_A, decreases with an increase in the concentration of Na_2mal, indicating that the number of the species in which mal^{2-} associates with two *trans* H_A through hydrogen bond, increases with increasing concentration of Na_2mal. However, the steady decrease of $k'_{t(s)}$ seems to indicate not the inaccessibility of general base to H_A but retardation due to ion-pairing offsetting the effect of general base catalysis.

For *cis* NH_2, an average of $k'_{c(H)}$ and $k'_{c(L)}$ increases up to 0.1 mol dm^{-3} of Na_2mal, though the increase is about one-fourth of that of $k'_{t(f)}$ at the same Na_2 mal concentration; the increments are 1.6 and 6.6 times for k'_c and $k'_{t(f)}$, respectively, as compared with the corresponding values in the absence of malonate. Although the increase of k'_c indicates that the malonate ion works as general base catalysis on *cis* NH_2, the effect on k'_c is smaller than that on $k'_{t(f)}$. This suggests that the malonate ion approaches *cis* NH_2 less frequently, which is quite likely from electrostatic consideration. The subsequent gradual decrease of k'_c may be explained in a manner similar to that for $k'_{t(f)}$.

The results can be summarized as follows. Malonate ion can work as general base catalyst for exchanging amine hydrogens. The values of $k'_{t(f)}$ for *trans* H_B and k'_c for *cis* NH_2 would be taken as a compromise of two opposing factors: rate acceleration due to general base catalysis by malonate ion and rate retardation due to ion-pairing (Fig. 3). The initial increase of $k'_{t(f)}$ and k'_c is due to general base catalysis and the subsequent gradual retardation to additional hydrogen bond effect. The steady decrease of $k'_{t(s)}$ for *trans* H_A caused by malonate ions is explained by the selective hydrogen bond between mal^{2-} and *trans* H_A.

Conformation of Ethylenediamine Chelates. With an increase in the concentration of Na_2mal, the ^1H signal of *cis* NH_2 split into two peaks, the separation increasing. In ^{13}C NMR spectra, both peaks assigned to en carbons underwent high field shifts by about 0.1 ppm upon addition of Na_2mal. This suggests that the conformational equilibrium of the two en chelates is driven toward either ($\delta\delta$) or ($\lambda\lambda$) by the presence of mal^{2-}.

The conformation of ethylenediamine coordinated to metal ions is rapidly interconverting between the δ and λ forms in aqueous solution.[15] If the conformations of two ethylenediamine rings are fixed as ($\delta\lambda$) or ($\lambda\delta$), the number of expected resonance peaks may be up to four for *cis* NH_2 on ^1H NMR spectra and also four for CH_2 resonance of en on ^{13}C NMR. However, the energy difference between ($\delta\lambda$) and ($\delta\delta$) or between ($\delta\lambda$) and ($\lambda\lambda$) is generally accepted as very small and the relative populations of these two conformations would be virtually 1 : 1. Thus the observed ^{13}C chemical shift, being an average with 1 : 1 weights, should be the midpoint between the shifts expected for the δ and λ conformers. On the other hand, if the conformation of two ethylenediamine is fixed as ($\delta\delta$) or ($\lambda\lambda$), the corresponding ^1H and ^{13}C spectra should consist of only two peaks. Since our system would be in rapid dynamical equilibrium between free and the associated species, and the conformation of en ring would be considered to be constrained by hydrogen bonding with mal^{2-} in the associated species, the observed spectra should be an average weighted by the abundance of respective species.

The signals split upon addition of malonate are not those with which malonate is proposed to be interacting, *i.e.*, *trans* NH_2. However, if we accept the view that conformational equilibrium is shifted to either ($\delta\delta$) or ($\lambda\lambda$) upon addition of malonate, the two kinds of hydrogens of *cis* NH_2 will have stereochemically different disposition, especially with respect to the cobalt-acac chelate; one of the *cis* NH_2 is poised over the chelate ring and the other is not. This will bring about a large chemical shift difference for the two *cis* hydrogens but not for the two *trans* ones. The effect of the magnetically anisotropic ring current of the chelate ring has not been clarified. However, the former hydrogen might be to a greater extent shielded than the latter.[16] On electrostatic grounds the *cis* NH poised over the chelate ring might undergo exchange more slowly. Experimentally, of the two *cis* signals the high field one is exchanged more slowly than the other, which is in line with our assumption.

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